ATTEMPTED SYNTHESIS OF PYRIDINE CONTAINING BIS-ALPHA-DIKETONES VIA THE BENZOIN CONDENSATION

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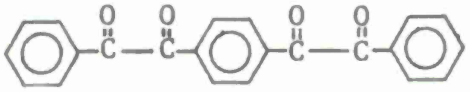
ABSTRACT

Although polyphenylquinoxalines are exceptional high-temperature-resistant resins, they are prohibitively expensive due largely to the high cost of the bis-α-diketones from which they are prepared. The benzoin condensation of each of the three isomeric pyridine monocarboxaldehydes with terephthaldehyde followed by oxidation has been investigated as an alternate route to these monomers. Although all such attempts were unsuccessful, an insight into the complexities of mixed benzoin condensations is presented.

INTRODUCTION

Although the polyphenylquinoxalines are among the best of the currently available high-temperature-resistant resins, they suffer the disadvantage of extremely high cost. This is due largely to the high cost of their aromatic bis-α-diketone monomers (e.g., I) which are prepared from expensive starting materials via a multistep synthesis.[1] Thus, a significant reduction in the cost of this monomer would have a similar effect on the polymer.



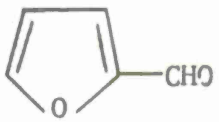
I

Although the benzoin condensation followed by oxidation has long been used for the preparation of aromatic α-diketones, extension of this route to the preparation of aromatic bis-α-diketones has been unsuccessful* (Eq.1).

(1)

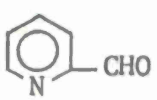
II III

Apparently, competing side reactions such as oligomerization of terephthaldehyde (III) and self condensation of benzaldehyde (II) prevent the desired mixed benzoin condensation from taking place. A recent report by Jones et al.,[2] however, has shown that the route can work when furan-2-carboxaldehyde (IV) is substituted for benzaldehyde.

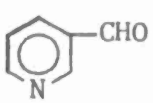


IV

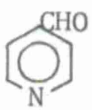
This result suggested the possibility of one or more of the isomeric pyridine monocarboxaldehydes (Va, b, and c) behaving in a similar manner.



Va



Vb



Vc

Since the thermal stability of the pyridyl group is comparable to that of the phenyl, the properties of polyquinoxaline(s) incorporating a pyridine-containing monomer should be essentially the same as the phenyl-containing analog. Thus, a successful preparation of pyridine containing bis-α-diketones using the inexpensive benzoin condensation route would provide a significantly less costly polyquinoxaline. Our efforts to develop such a route are described.

*PACIOREK, K. L., KARLE, D. W., and KRATZER, R. H. *Synthesis of Isomeric Bisbenzils.* Ultrasystems, Inc., Contract N00017-73-C-4325, Final Report, August 1974. This report, which appeared while the present work was in progress, describes a successful application of the benzoin condensation to the synthesis of aromatic bis-α-diketones.

1. WRASIDLO, W. J., and AUGL, J. M. *Synthesis and Evaluation of New Phenylated Polyquinoxalines.* Naval Ordnance Laboratory, NOL TR 69-120, October 1969.
2. JONES, R. J., VAUGHAN, R. W., O'RELL, M. K., and SHEPPARD, C. H. *Development of Autoclavable Addition-Type Polyimides.* TRW Systems Group, Contract NAS3-15834, Final Report, NASA CR-121251, February 1974.

EXPERIMENTAL

Materials

The 2-, 3-, and 4-pyridinecarboxaldehydes (Aldrich) were vacuum distilled, stored under nitrogen, and refrigerated. Terephthaldehyde (Aldrich) was washed with $NaHCO_3$, and recrystallized from 50% $EtOH/H_2O$. Dibenzo-18-crown-6 was prepared according to the literature, mp 163 to 165 C (Reference 3, 164 C). Hexamethylphosphoramide, N,N-dimethylformamide and acetonitrile were redistilled and dried (molecular sieves). All other compounds were used as received. Melting points (uncorrected) were taken on a Fisher-Johns melting point apparatus and infrared spectra were recorded on a Perkin-Elmer Model 137 Spectrophotometer.

CONDENSATION

Aqueous

An ethanolic solution of the desired amounts of terephthaldehyde and the particular pyridine carboxaldehyde was placed in a round bottom flask fitted with a magnetic stirrer and a reflux condenser capped with an addition funnel. To this was added dropwise with stirring a saturated solution of the required amount of KCN in ethanol/water (1:1,v:v). The reaction time and temperature were varied according to the experiment, depending upon the reactivity of the pyridinecarboxaldehyde. After the time indicated (Table 1), the mixture was cooled (if above ambient) and poured with stirring into a 5-fold excess of water. The resulting solids were removed by filtration, water washed, and finally air dried. In some cases recrystallization from ethanol or chloroform was attempted.

Nonaqueous

Crown Ether Method

An acetonitrile solution of terephthaldehyde and 2-pyridinecarboxaldehyde was placed in a three-neck round bottom flask fitted with a mechanical strirrer, a reflux condenser, and an addition funnel. To this was added dropwise with stirring an acetonitrile solution of the required quantity of dibenzo-18-crown-6/KCN complex. After one hour the precipitate, if present, was removed by filtration, dried, and recrystallized from ethanol. In those cases where no solid was present, the solution was taken to dryness with a rotary evaporator. The resulting solids were triturated with water in order to break down the KCN/crown ether complex. This crude product was subjected to oxidation (see below).

N,N-Dimethylformamide Method

An N,N-dimethylformamide solution of terephthaldehyde and 2-pyridinecarboxaldehyde was placed in a three-neck round bottom flask equipped with a mechanical stirrer, a reflux condenser, and an addition funnel. To this was added dropwise with stirring a saturated solution of the required amount of KCN in N,N-dimethylformamide. After stirring for 24 hours, the reaction mixture was poured with

3. PEDERSEN, C. J. *Cyclic Ethers and Their Complexes with Metal Salts.* Journal of the American Chemical Society, v. 89, 1967, p. 7017-36.

stirring into a 5-fold excess of water. The resulting solids were removed by filtration, water washed, and vacuum dried. This crude product was subjected to oxidation.

Table 1. CONDENSATIONS

Exp.	Pyridine Aldehyde	Mole Ratio (a)	Mole Ratio (b)	Reaction Conditions: Solvent System	Reaction Conditions: Time (hr)	Reaction Conditions: Temp.	Oxidation	Comments
1	4	2:1	1:1	EtOH/H_2O	0.5	reflux		Very poor yield crude product, no identifiable bis-benzoin
2	4	2:1	4:1	EtOH/H_2O	2.0	reflux	Table 2 Exp. 1	Crude yield higher, recrystallized fraction oxidized
3	2	2:1	4:1	EtOH/H_2O	2.0	reflux		α-pyridoin only product identified
4	2	2:1	4:1	EtOH/H_2O	0.25	ambient		Red and yellow materials isolated, neither bis-benzoin
5	2	2:1	3:1	EtOH/H_2O	0.25	0 C		No bis-benzoin isolated
6	2	2:1	1:1	MeCN Crown ether	1.0	ambient		No bis-benzoin isolated
7	2	2:1	1:10	MeCN Crown ether	1.0	ambient	Table 2 Exp. 2	Crude product subject to oxidation
8	2	2:1	1:1	DMF	24.0	ambient	Table 2 Exp. 3	Crude product subject to oxidation
9	3	2:1	4:1	EtOH/H_2O	24.0	ambient		Product mp 187 to 190 C, poor elemental analysis for bis-benzoin*†
10	3	2:1	4:1	EtOH/H_2O	24.0	70 C		Same product as in Exp. 9
11	3	4:1	3:1	EtOH/H_2O	24.0	ambient	Table 2 Exps. 4, 5&6	Product mp 154 to 155 C, elemental analysis*‡ fails to comfirm bis-benzoin

*Calcd. for $C_{20}H_{16}N_2O_4$: C, 69.0; H, 4.6; N, 8.0; O, 18.4
†Found: N, 6.3
‡Found: C, 65.8; H, 5.3: N, 8.6
(a) Pyridine Aldehyde/Terephthaldehyde
(b) KCN/Terephthaldehyde

OXIDATIONS

Copper Sulfate-Pyridine Method

In a round bottom flask equipped with a magnetic stirrer and a condenser was placed a solution of the required amount of $CuSO_4 \cdot 5H_2O$ in 70:30 pyridine:water (v:v) and the presumed bis-benzoin (see above). After reaction (see Conditions, Table 2), the mixture was poured with stirring into a 5-fold excess of water. The resulting precipitate was removed by filtration, water washed, and dried. In those cases where recrystallization was attempted, ethanol was used.

Copper Sulfate-Hexamethylphosphoramide Method[4]

To a magnetically stirred solution of the required amount of $CuSO_4 \cdot 5H_2O$ in hexamethylphosphoramide in a round bottom flask was added the presumed bis-benzoin in one portion. The resulting mixture was stirred for the desired period (see Table 2) while oxygen was slowly bubbled through in order to maintain the copper in the 2^+ oxidation state. The resulting bright green mixture was poured with stirring into a 5-fold excess of water. The resulting solids were removed by filtration, water washed, and dried. Attempted recrystallization from several solvents failed to yield the desired bis-α-diketone.

Table 2. OXIDATIONS

Exp.	Substrate Table 1 Exp.	Oxidant Solvent	Reaction Conditions Time (hr)	Temp.	Comments
1	2	$CuSO_4$/pyridine*	5.0	reflux	Green material isolated. No isolation of bis-α-diketone.
2	7	$CuSO_4$/pyridine*	5.0	reflux	Yellow material isolated. Unpurified by chromatography or recrystallization.
3	8	$CuSO_4$/pyridine*	24.0	ambient	Isolation of α-pyridil and other unidentified material.
4	11	$CuSO_4$/HMPA*	24.0	ambient	Green material isolated. No isolation of bis-α-diketone,
5	11	10%HNO_3/AcOH	1.0	100 C	Recovery of starting material only.
6	11	50%HNO_3/AcOH	1.0	100 C	Isolation of presumed carboxylic acids.

*The concentration of $CuSO_4$ in this experiment was in a four-mole excess based on presumed pure bis-benzoin.

4. MACAIONE, D. P., and WENTWORTH, S. E. *An Improved Method for the Synthesis of Benzils from Benzoins.* Synthesis, 1974, p. 716.

Nitric Acid Method

The presumed bis-benzoin was dissolved in an acetic-acid/nitric-acid mixture (see Table 2) in a round bottom flask fitted with a magnetic stirrer and a reflux condenser. After stirring for one hour under reflux, the reaction mixture was cooled and diluted with one third its volume of water. The resulting solids were isolated by filtration, water washed, and air dried.

DISCUSSION

4-Pyridinecarboxaldehyde

The condensation of 4-pyridinecarboxaldehyde with terephthaldehyde in aqueous ethanol, the usual solvent for the benzoin condensation (Table 1, Exp. 1) yielded products in such small quantity that purification and identification were impossible. An increase in the concentration of KCN according to the procedure of Jones et al.[2] (Table 1, Exp. 2) led to an increased yield which still resisted purification. A possible source of this difficulty is the number of isomeric forms, both positional and stereo, in which the bis-benzoin can exist. However, since all of these isomers can be oxidized to the same desired bis-α-diketone, a portion of this impure material was subjected to oxidation with copper sulfate in pyridine (Table 2, Exp. 1). Unfortunately, this procedure yielded only a green unrecrystallizable copper-containing material which was presumed to be complex. At this point it was decided to proceed to the 2-pyridinecarboxaldehyde system.

2-Pyridinecarboxaldehyde

Attempted condensation of 2-pyridinecarboxaldehyde and terephthaldehyde using the procedure of Jones et al.[2] (Table 1, Exp. 3) gave α-pyridoin as the only isolable product. It was noted that the initially burgundy colored reaction mixture took on an orange color typical of α-pyridoin as the reaction progressed. It was speculated that the burgundy color might be due to the desired bis-benzoin which, on heating in the presence of KCN, reverted to the thermodynamically more stable α-pyridoin. Accordingly, this reaction was attempted at ambient and subambient temperatures (Table 1, Exps. 4 and 5) for a shorter time. Unfortunately, although the red color was retained in both cases, neither attempt yielded the desired bis-benzoin. The infrared spectrum of the water washed and dried products indicated the presence of both hydroxyl and nitrile groups from which we infer the presence of a cyanohydrin, the conjugate base of which has been suggested as an intermediate in the benzoin condensation.[5] We next sought to enhance the catalytic activity of the cyanide ion through complexation of its potassium counter-ion with dibenzo-18-crown-6 (a cyclic or so-called crown ether) (Table 1, Exps. 6 and 7). In neither case was a bis-benzoin isolated. The crude product from Exp. 7 was subjected to oxidation with copper sulfate/pyridine (Table 2, Exp. 2). This reaction failed to yield the desired bis-α-diketone. In the hope that a simple nonaqueous solvent might facilitate this condensation, it was run in N,N-dimethylformamide (Table 1, Exp. 8). Subsequent oxidation of the crude product (Table 2, Exp. 3) yielded only α-pyridil.

5. IDE, W. S., and BUCK, J. S. *The Synthesis of Benzoins.* Organic Reactions, v. 4, 1948, p. 273-4.

3-Pyridinecarboxaldehyde

When the procedure of Jones et al.[2] was applied to the condensation of 3-pyridinecarboxaldehyde and terephthaldehyde (Table 1, Exp. 9), a product was obtained whose infrared spectrum and melting point was consistent with that of a bis-benzoin. Elemental analysis, however, failed to confirm the desired structure. Repeat of this reaction at elevated temperature (Table 1, Exp. 10) yielded the same product. When the reaction was run with a 2-fold excess of 3-pyridinecarboxaldehyde (Table 1, Exp. 11), a lower melting product was obtained whose infrared specturm again supported a bis-benzoin structure. Although the elemental analysis was closer to that required for the desired bis-benzoin, it still failed to confirm that structure. Oxidation of this material under a variety of conditions (Table 2, Exps. 4, 5, and 6) failed to yield the desired bis-α-diketone.

CONCLUSIONS

As can be seen from an inspection of Table 1, an appropriate set of conditions for the benzoin condensation of pyridinecarboxaldehydes with terephthaldehyde has not been discovered. Although the method developed by Paciorek et al. might be effective with this system, their success with benzaldehyde in this reaction clearly eliminates economics as a rationale for further investigation of heterocyclic bis-α-diketones.

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